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(54) FERROELECTRIC CERAMIC, PYROELECTRIC AND PYROELECTRIC INFRARED RAY DETECTOR

(57)Abstract:
PROBLEM TO BE SOLVED: To impart an excellent quality factor to a pyroelectric consisting of a solid solution of lead zirconate, lead titanate and magnesium lead niobate and a ceramic doped with manganese or the like.
SOLUTION: A ferroelectric ceramic consisting of the solid solution of lead zirconate, lead titanate and magnesium lead niobate, doped with manganese or the like to control the electrical conductivity, having a composition expressed by a formula, Pb1+. (((Mg1/3Nb2/3)y(Zr1-xTix)1-y)1-zAz)O3 and used as the pyroelectric is prepared. In the formula, each of ., x, y and z is 0.05 ≥. ≥0 and preferably 0.02≥. >0, 0.4≥x>0 and preferably 0.25≥x>0, 0.4≥y>0 and preferably 0.24≥ y>0, 0.05≥z>0 and 0.88≥(1-x)(1-y), A represents a cationic polyvalent octagonal site substituting group, is manganese or uranium and substitutes Mg, Nb, Zr and Ti on the perovskite lattice site by oxygen ion forming octagonal coordination.

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【外国語明細書】

1 Title of Invention

FERROELECTRIC CERAMICS, PYROELECTRICS AND PYROELECTRIC INFRA RED DETECTOR

2 Claims

1. A ferroelectric ceramic for use as a pyroelectric, said ceramic having the composition:

$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y(Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3$

where: $0.05 \geq \delta \geq 0$

$0.4 \geq x > 0$

$0.4 \geq y > 0$

$0.05 \geq z > 0$

and wherein A is a cationic multivalent octahedral site substituent.

2. A ferroelectric ceramic according to claim 1, wherein:

$0.88 \geq (1-x)(1-y)$

3. A ferroelectric ceramic according to claim 1 or 2, wherein

$0.25 \geq x > 0$

$0.24 \geq y > 0$

4. A ferroelectric ceramic according to claim 1, 2 or 3, wherein A is manganese.

5. A ferroelectric ceramic according to claim 1, 2 or 3, wherein A is uranium.

6. A ferroelectric ceramic according to claim 1, wherein:

$x=0.125\pm0.01$, $y=0.025\pm0.01$, $z=0.01\pm0.002$ and A=Mn

7. A ferroelectric ceramic according to claim 1, wherein:

$x=0.075\pm0.01$, $y=0.075\pm0.01$, $z=0.01\pm0.002$ and A=Mn

8. A ferroelectric ceramic according to claim 1, wherein:

$x=0.175\pm0.005$, $y=0.025\pm0.005$, $z=0.0065\pm0.001$ and A=U

9. The use of a ferroelectric ceramic according to any preceding claim as a pyroelectric.

10. A pyroelectric infra red detector having an active pyroelectric material which is a ferroelectric ceramic according to any one of claims 1 to 8.

11. A pyroelectric infra-red detecting device comprising a plurality of detector elements in the form of a two dimensional array linked to a silicon multiplexer amplifier chip, wherein the detector elements comprise an active material which is a ferroelectric ceramic according to any one of claims 1 to 8.

12. The use of a ferroelectric ceramic as a pyroelectric, said ferroelectric ceramic having the composition:

$$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y(Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3$$

where: $0.05\geq\delta\geq0$

$1>x>0$

$1>y>0$

$0.05\geq z>0$

and wherein A is a cationic multivalent octahedral site substituent.

13. A pyroelectric infra red detector having an active pyroelectric material which is a ferroelectric ceramic having the composition:

$$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y(Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3$$

where: $0.05\geq\delta\geq0$

$1>x>0$

$1>y>0$

$0.05 \geq z > 0$

and wherein A is a cationic multivalent octahedral site substituent.

14. A pyroelectric infra-red detecting device comprising a plurality of detector elements in the form of a two dimensional array linked to a silicon multiplexer amplifier chip, wherein the detector elements comprise an active material which is a ferroelectric ceramic having the composition:

$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y(Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3$

where: $0.05 \geq \delta \geq 0$

$1 > x > 0$

$1 > y > 0$

$0.05 \geq z > 0$

and wherein A is a cationic multivalent octahedral site substituent.

3 Detailed Description of Invention

This invention relates to ferroelectric ceramics.

The use of ferroelectric ceramics as the active detector material for pyroelectric infra-red (IR) detectors is known. The range of pyroelectric devices and the various single crystal, polymeric and ceramic materials which have been used as the active material in them is described in detail in, for example, a paper by R.W. Whatmore ((1986) "Pyroelectric Devices and Materials" Rep. Prog. Phys. 49 1335-1386). This reference also discloses the figures-of-merit which can be used to decide whether-or-not one material is more-suitable than another for a particular type of pyroelectric device. These figures-of-merit are various combinations of the physical properties of the pyroelectric material and are directly related to the performance of the devices of interest. The most commonly-used figures-of-merit are:

$$F_i = p/c' \qquad (1)$$

where the current responsivity of the device is proportional to F_i

$$F_v = p/(c'\varepsilon_0\varepsilon) \qquad (2)$$

where the voltage responsivity of the device is proportional to F_v

$$F_D = p/(c'(\varepsilon_0\varepsilon\tan\delta)^{0.5}) \qquad (3)$$

where the specific detectivity of the device is proportional to F_D

In these formulae:

p = pyroelectric coefficient

c' = volume specific heat

ε = dielectric permittivity at the frequency of device operation

$\tan\delta$ = dielectric loss tangent at the frequency of device operation

ε_o = dielectric permittivity of free space

In an ideally-matched pyroelectric device the input capacitance of the amplifier linked to the pyroelectric element would be similar in magnitude to that of the element

itself. In this case, the figure-of-merit F_D is the most important one to use. In devices where the element capacitance is much larger than the amplifier capacitance, or where the AC Johnson Noise in the element does not dominate in the noise figure for the device, F_v is the appropriate figure-of-merit to use. In cases where the element capacitance is much smaller than the amplifier capacitance, then F_i is the appropriate figure-of-merit to use.

Table 1 shows the pyroelectric properties of some of the commercially-available materials for pyroelectric applications (taken from reference 1). All the commercial pyroelectric ceramic materials are based upon modifications to the perovskite ceramic solid solution system lead zirconate - lead titanate ($PbZrO_3$-$PbTiO_3$ - hereinafter called "PZT"). The vast majority of these are based upon lead titanate ($PbTiO_3$ - hereinafter called "PT"). An example is the composition $(Pb_{1-x}Ca_x)((Co_{1/2}W_{1/2})_yTi_{1-y})O_3$ with x=0.24, y=0.04 which was described in a paper by N. Ichinose ((1985) Am. Ceram. Soc. Bull. 64 1581-1585). Typical properties for such ceramics are listed under the heading of "modified PT" given in Table 1. These values have been measured on a modified lead titanate ceramic manufactured by Morgan Matroc Unilator Division and known as PC6.

A particular commercial family of pyroelectric ceramics has also been developed based upon PZT compositions close to lead zirconate, ($PbZrO_3$ - hereinafter called "PZ") in this case in solid solution with lead iron niobate ($PbFe_{0.5}Nb_{0.5}O_3$) which was described in a paper by R.W. Whatmore and A.J. Bell ((1981) Ferroelectrics 35 155-160). In this case uranium is added as a dopant to control the electrical conductivity. The properties of this ceramic, which is supplied commercially by GEC Marconi Materials Technology are listed in Table 1 under heading "Modifed PZ".

Other authors have described ceramic compositions which are particularly suitable for piezoelectric applications. A paper by H. Ouchi, K. Nagano and S. Hayakawa ((1965) J. Amer. Ceram. Soc. 48 (12) 630 - 635) discloses the piezoelectric and high frequency (>1KHz) dielectric properties of compositions throughout the phase diagram. The compositions disclosed in this reference are based on PZ, PT and lead magnesium niobate (hereinafter called "PMN"). It should be noted that none of the properties reported in this reference would be of-use in predicting the properties of a

pyroelectric device using them. While the dielectric properties (permittivity and loss) might at first sight seem useful in providing some data for the computation of pyroelectric figures-of-merit, according to the formulae given here, the frequency at which the properties are measured should be in the same range as those used in practical pyroelectric devices (usually <100Hz). This is particularly important for the dielectric loss, which can rise rapidly as the frequency is reduced below 100Hz. Compositions cited in this reference are shown in the PZ-PT-PMN ternary phase diagram shown in Figure 1.

A paper by H. Ouchi, M. Nishida and S. Hayakawa ((1966) J. Amer. Ceram. Soc. 49 (11) 577 - 582) discloses the piezoelectric and high frequency (>1KHz) dielectric properties of a much more restricted set of compositions of the form $Pb[(Mg_{1/3}Nb_{2/3})_{0.375}Zr_{0.375}Ti_{0.25}]O_3$ with small additions (0.2 to 1.0 mole %) of Cr_2O_3, Fe_2O_3 or NiO.

A paper by H. Ouchi ((1968) J. Amer. Ceram. Soc. 51 (3) 169 - 176) discloses the piezoelectric and high frequency (>1KHz) dielectric properties of compositions in the PZ-PT-PMN ternary system with small (up to 10 mole %) substitutions of Ba or Sr for Pb. None of these papers describes the pyroelectric or low frequency dielectric properties, which would be relevant to the applications in pyroelectric infra-red detectors.

Three papers have also been published which describe the pyroelectric properties of ceramics in related compositional systems. These are by: M. Kobune, S, Fujii and K. Asada ((1984) J. Ceram. Soc. Japan 104 (4) 259-263); S.W. Choi, S.J. Jang and A. Bhalla ((1989) J. Korean Physical Society 22 (1) 91-6); and M.M. Abou Sekkina and A. Tawfik (1984) J. Mat. Sci. Let. 3 733-738. The first of these (Kobune et al) discloses the pyroelectric properties of ceramics with the compositions: $PbZr_xTi_{1-x}O_3$-0.5Wt.%Mn0 with x=0.1 to 0.5. These compositions contain no PMN, and the crystal structure of the compositions described by this reference are tetragonal.

Choi et al discloses the pyroelectric properties of ceramics in the $(1-X)Pb(Mg_{1/3}Nb_{2/3})O_3$-$XPbTiO_3$ solid solution. Here again, the crystal structure exhibited by of all the ceramics described is tetragonal. Furthermore, the structures contain no PZ. Finally, Abou Sekkina and Tawfik discloses the pyroelectric properties of ceramics with the composition $Pb_{1-y/2}(Zr_{1-(x+y)}Ti_xNb_y)O_3$. Here, the ceramics are

rhombohedral but contain no Mg.

Pyroelectric ceramic materials are disclosed in Japanese patent publication nos. JP-01264962 and JP-020051426. Piezoelectric ceramics are described in European patent publication no. EP-A-0484231.

The present invention relates to new ceramic compositions for use in pyroelectric applications, which have been shown to possess particularly good pyroelectric figures-of-merit. The properties, in fact, can exceed those of the modified PT and PZ ceramics described earlier. The ceramic is a composition comprising a solid solution between lead zirconate (PZ), lead titanate (PT) and lead magnesium niobate (PMN), doped with other elements such as manganese for electrical conductivity control. The compositions according to the invention are rhombohedral in structure.

The composition of the ceramic can be described by the following chemical formula:

$$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y (Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3 \qquad (4)$$

where: $0.05 \geq \delta \geq 0$

$0.4 \geq x > 0$

$0.4 \geq y > 0$

$0.05 \geq z > 0$

where A is a cationic multivalent octahedral site substituent such as manganese or uranium.

The cationic multivalent octahedral site substituent possesses multiple valency, and substitutes for Mg, Nb, Zr or Ti on the perovskite lattice site which is octahedrally coordinated by oxygen ions. Furthermore, the substituent is not valence-balanced by another simultaneous B-site substituent of higher or lower valency (e.g. Mn and Nb in the ratio of 1:2).

The preferred regions of the PMN-PZ-PT phase diagram are marked on the ternary phase diagram given in figure 2. (Note that this diagram assumes z=0 in the above formulation. The way the composition is formulated, small additions of z can be made without changing the relative proportions of PMN, PZ or PT.)

Within the compositional range (4) defined above, the range:

$$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y (Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3 \qquad (5)$$

where: $0.05 \geq \delta \geq 0$, preferably $0.02 \geq \delta > 0$

$0.25 \geq x > 0$

$0.24 \geq y > 0$

$0.88 \geq (1-x)(1-y)$

$0.05 \geq z > 0$

is of particular interest for pyroelectric applications.

The following compositions are especially preferred:

$x = 0.125 \pm 0.01$, $y = 0.025 \pm 0.01$, $z = 0.01 \pm 0.002$, A=Mn;

$x = 0.075 \pm 0.01$, $y = 0.075 \pm 0.01$, $z = 0.01 \pm 0.002$, A=Mn;

$x = 0.175 \pm 0.005$, $y = 0.025 \pm 0.005$, $z = 0.0065 \pm 0.001$ and A=U.

The small excess of lead, represented by the parameter δ in the above formula (4) and (5) has two effects. The first is to compensate for small losses of Pb by evaporation during sintering (see below). The second is that, together with the level of the off-valent dopant, it will have the effect of controlling the electrical conductivity of the sintered body. If $z \geq 0.002$ reducing δ will tend to reduce conductivity and vice-versa.

It should be noted that the relative proportions of the starting materials do not change during the production process, with the exception of the small losses of PbO caused by evaporation.

In practice, both x and y are usually greater than 0.01, and are preferably greater than 0.02. Furthermore, z is typically greater 0.001, and is preferably greater than 0.002. It is preferred that z is less than 0.02.

In another aspect, the invention provides the use as a pyroelectric of compositions comprising PMN-PZ-PT doped with a cationic multivalent octahedral site substituent such as manganese or uranium. Preferably, the PMN-PZ-PT ceramics have the composition described above.

The invention also provides a pyroelectric infrared detector having a pyroelectric material comprising PMN-PZ-PT doped with a cationic multivalent octahedral site substituent such as manganese or uranium. Preferably, the PMN-PZ-PT ceramics have the composition described above.

In another aspect the invention provides a pyroelectric infrared detecting device

comprising a plurality of detector elements in the form of a two dimensional array linked to a silicon multiplexor amplifier chip. The active material in pyroelectric detector elements comprises PMN-PZ-PT doped with a cationic multivalent octahedral site substituent such as manganese or uranium. Preferably, the PMN-PZ-PT ceramics have the composition described above.

Reference is now made to the accompanying drawings, in which:

Figure 1 is a ternary phase diagram for PZ-PT-PMN showing compositions described by H. Ouchi, K. Nagano and S. Hayakawa in the paper described (Ouchi 1995), and showing compositions described in other papers discussed above; and

Figure 2 is a ternary phase diagram for PZ-PT-PMN showing the regional specified in formula (4) above and the regions specified in formula (5) above.

It should be noted that in Figure 2 it is assumed that $z = 0$. The composition is formulated in such a way that small additions of z can be made without changing the relative proportions of PMN, PZ or PT. It should also be noted that in Figure 2, formula (4) has been modified so that x and y are greater than 0.01, and formula (5) has been modified so that x and y are greater than 0.02.

There will now be described a way of making ceramics in accordance with the invention. It will be appreciated that the ceramics according to the invention may be made by other methods.

The composition selected is used to calculate the amounts of starting compounds which are required to make the final material. The usual starting compounds are basic magnesium carbonate ($MgCO_3.6H_2O$), niobium pentoxide (Nb_2O_5), titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), lead monoxide (PbO) and manganese dioxide (MnO_2). In each case it is highly desirable to use very finely divided powders for the fabrication and to ensure that the powders are at least 99.9% purity. Alternative starting materials are discussed below.

The basic magnesium carbonate and niobium pentoxide powders are first weighed in equi-molar proportions and placed in a cylindrical receptacle (ball mill) filled with hard balls or cylinders (the milling medium) and a fluid medium for a process known as ball milling. In a specific, and optimum, example, the cylinders are made out of a ceramic known as yttria-stabilised zirconia and the medium is pure water, and the

ball mill is made of polyethylene. A commercial dispersant such as "Dispex" can be added to aid the ball milling process. Alternatively, the milling medium can be acetone, the ball mill made of rubber lined steel and the milling medium steel balls. Any combination of these could be used successfully in this embodiment of the invention. The powders are ball-milled for 6 hours, although a period between 4 and 12 hours would be successful. The resulting slurry is taken out of the ball mill and placed in a flat tray in an oven at between 60 and 90 °C to dry. As an alternative, the slurry can be dried in a spray-dryer. The resulting powder is sieved through a 200 μm mesh sieve and placed in a crucible inside a furnace at a temperature between 800 and 990 °C for a period between 4 and 12 hours. The resulting compound is $MgNb_2O_6$. This is used as a starting oxide for making the required ceramic powder.

A specific example of how to process a composition with x=0.075, y=0.075, z=0.01, δ=0.01 will now follow:

The following weights of powders should be used:

Compound	Weight (g)
PbO	56.355
TiO_2	1.372
ZrO_2	26.094
$MgNb_2O_6$	1.894
MnO_2	0.217

Clearly, this is an example and any weights of the powders can be used as long as they are kept in the above proportions by weight.

The powders are weighed-out into a ball mill of the type described above and ball milled for a period of between 4 and 12 hours, with 6 hours being the optimum, using water with a suitable dispersant as the milling medium. The resulting slurry is dried as described above, sieved and the powders are placed in an alumina crucible and heated to between 800 and 900 °C for between 4 hours, with 6 hours being the optimum. This process is known as calcination.

After calcination, the powders are again placed in a ball mill and ball milled for a period of between 6 and 24 hours, with 18 hours being the optimum, using water with a suitable dispersant as the milling medium. For the last hour of the milling process an organic polymer is added to the milling slurry. This binder can be a range of commercial materials, but a suitable example is a 50% mixture of polyvinyl alcohol and polyethylene glycol in water as solvent. The binder is typically added to the slurry at a proportion of between 2 and 6 percent by weight of the powder present in the slurry. The resulting slurry is dried as described above, with frequent stirring if in a flat tray, the resulting stock powder is sieved and placed in a suitable receptacle for storage.

The stock powder is used to make the ceramic in the following fashion. In the first example, the stock powder is placed in a steel punch and die set and compressed to form a "green" pellet of the required dimensions. Typically the pressure used to achieve this would be between 100 and 160 MPa. Typically, several pellets would be pressed and processed simultaneously. The pellets are first placed side-by side on an open alumina tray in a furnace and heated slowly (typically 300 °C/hour) to a temperature of between 500 and 700 °C. This process eliminates the binder from the compacts. These compacts, which are then said to be "biscuited", are stacked on top of each other on top of an alumina plate which has been lapped flat. Typically, a fine layer of a calcined lead zirconate powder is placed between each compact to stop them sticking together during the sintering process. Alternatively, thin platinum foil can be used for this task. An alumina crucible whose edges have also been lapped flat to make a good seal to the alumina plate is then placed over the compacts. In a further variation of the process, pre-calcined lead zirconate powder or a powder of the same composition as the compacts can be placed inside the crucible assembly. The whole assembly is placed inside a furnace and heated to a temperature of between 1200 and 1290 °C for a time of between 2 and 8 hours. Heating and cooling rates are typically 600 °C/hour. This completes the sintering process. The resulting sintered ceramic pellets can then be separated, cleaned and cut into wafers of the required dimensions using a diamond saw.

In other embodiments of this invention, the stock powder can be formed into pellets using cold isostatic pressing. Alternatively, the powder can be formed into

plates or sheets using a process such as tape casting or other shaped bodies by injection moulding. In the latter cases, other binders, well known to those skilled in the art would be used to form the green bodies. In any case, the green bodies would be biscuited and sintered as described above. Other processes which can be applied to make the sintered bodies would be hot uniaxial or hot isostatic pressing.

The ceramic wafers or bodies produced using one of the processes discussed above must have electrodes applied and be subject to the process known as electrical poling before they can be used in practical devices. Electrodes can be applied to wafers or discs using one of a variety of processes. A typical process would be to paint silver powder dispersed in an organic medium onto both surfaces of a wafer. This will make a conducting layer which can be made more durable if a small proportion of glass is included in the electrode by firing the wafer, typically at 700 °C. Alternatively, an electrode such as a thin (typically 5nm) layer of chromium, topped by a thicker (typically 100nm) layer of gold can be used. These can be deposited using one of a number of physical vapour deposition methods such as thermal evaporation or sputtering, again well known to those skilled in the art. The electroded wafer is placed in a medium designed to have a high electrical breakdown strength, such as paraffin oil, and heated to a temperature of between 100 and 150 °C. An electrical potential difference of 3000 V per mm of sample thickness is applied to the sample electrodes and the sample is cooled to room temperature over a period of typically 15 to 60 mins. After this, the samples can be cleaned in suitable solvents. This completes the poling process.

The relevant properties obtained from a selection of ceramic specimens contained within the range defined above will now be described. A set of compositions and the weight proportions of the oxides going to make them up is described in Table 2. Table 3 lists the electrical properties of some of these compositions. Of these, compositions 3 and 6 are particularly interesting for pyroelectric applications.

Table 4 shows an example of the effect of uranium substitution on DC electrical resistivity for a set of composition compared with a similar composition doped with Mn.

Examples will now be given of methods which can be used for making pyroelectric detectors of electromagnetic radiation using the materials described above. After electrical poling, the wafers are lapped and polished to thicknesses of between

20 and 200 μm, the precise value determined by the performance required from the device. An electrode is applied, typically the evaporated or sputtered chromium/gold combination as described above to one face (the back face) of the wafer and a nickel/chromium alloy electrode possessing a surface resistivity of 377 Ω/square to the other (front) face. This is the face exposed to the radiation to be detected in the final device. The wafer is then cut into detector elements, typically squares of between 100 μm and 5 mm on a side, and the elements are placed inside a package with a high input impedance amplifier and suitable electrical biasing circuitry. The package is designed to have a front window which is transparent to the radiation to be detected. Typically, but not exclusively, this would be infra-red radiation with a wavelength of between 3 μm and 14 μm and the window would be a material such as silicon or germanium with a thin-film radiation-wavelength selective filter deposited on it.

As a further variant, the pyroelectric device can consist of a plurality of detector elements in a two-dimensional array in which each element is equipped with its own amplifier and all the amplifier outputs are linked to a multiplexer circuit, all integrated onto one piece of silicon. In this case the pyroelectric ceramic wafer has many element electrode areas defined upon it by photolithography and each element must be linked to the input of an amplifier by the means of a suitable interconnection technology such as one of the flip-chip hybridisation methods (e.g. solder bump, gold bump or conducting epoxy bump) which are well known to those skilled in the art of semiconductor device interconnection.

It will be appreciated that the invention described above may be modified.

【表1】

Material	Type	p	Dielectric Properties at 33Hz		c'	F_V	F_D
		10^{-4} $Cm^{-2}K^{-1}$	ε	$\tan\delta$	10^{6} $Jm^{-3}K^{-1}$	$m^{2}C^{-1}$	10^{-5} $Pa^{-1/2}$
Modified PZ	Ceramic	4	300	0.014	2.5	0.06	2.6
Modified PT	Ceramic	3.5	220	0.03	2.5	0.08	1.9

Table 1

Properties of some typical commercial pyroelectric materials

【表２】

Comp. No.	Code	100x δ	100x x	100x y	100x z	PbO Wt (g)	TiO2 Wt (g)	ZrO2 Wt (g)	MgNb2O6 Wt (g)	MnO2 Wt (g)	Total Wt (g)
2	P101MNZTM7.5/2.5/1	1	7.5	2.5	1	56.355	1.446	27.504	0.631	0.217	86.154
3	P101MNZTM12.5/2.5/1	1	12.5	2.5	1	56.355	2.410	26.018	0.631	0.217	85.631
6	P101MNZTM7.5/7.5/1	1	7.5	7.5	1	56.355	1.372	26.094	1.894	0.217	85.932
7	P101MNZTM12.5/7.5/1	1	12.5	7.5	1	56.355	2.286	24.683	1.894	0.217	85.436
8	P101MNZTM2.5/12.5/1	1	2.5	12.5	1	56.355	0.432	26.018	3.157	0.217	86.180
9	P101MNZTM7.5/12.5/1	1	7.5	12.5	1	56.355	1.297	24.683	3.157	0.217	85.710
10	P101MNZTM7.5/7.5/0.5	1	7.5	7.5	0.5	56.355	1.378	26.226	1.904	0.109	85.972
11	P101MNZTM7.5/7.5/1.5	1	7.5	7.5	1.5	56.355	1.365	25.962	1.884	0.326	85.893
21	P101MNZTM12.5/12.5/1	1	12.5	12.5	1	56.355	2.162	23.349	3.157	0.217	85.241

Table 2

Relative weights of oxides constituent in the ceramics described in this patent.

【表３】

Composition No.	Code	Resistivity $10^9\Omega.m$	Dielectric Constant (33Hz)	Dielectric Loss Tang. (33Hz)	Pyroelectric Coefficient $10^{-4}Cm^{-2}K^{-1}$	F_v $10^{-2}m^2C^{-1}$	F_D $10^{-5}Pa^{-0.5}$
2	P101MNZTM7.5/2.5/1	1.0	188	0.0072	2.81	6.80	3.26
3	P101MNZTM12.5/2.5/1	1.1	196	0.0049	3.08	7.10	4.23
6	P101MNZTM7.5/7.5/1	8.30	192	0.0065	3.17	7.46	3.81
7	P101MNZTM12.5/7.5/1	3.46	217	0.0095	3.05	6.35	2.88
8	P101MNZTM2.5/12.5/1	3.47	266	0.017	2.22	3.77	1.40
9	P101MNZTM7.5/12.5/1	152.00	218	0.0073	3.56	7.38	3.79
10	P101MNZTM7.5/7.5/0.5	665.00	231	0.006	3.05	5.96	3.48
11	P101MNZTM7.5/7.5/1.5	0.29	173	0.006	3.13	8.17	4.13
21	P101MNZTM12.5/12.5/1	0.55	260	0.014	2.58	4.48	1.82

Table 3

Electrical properties of some selected ceramic compositions

【表４】

Sample Code	A	x	y	z	Resistivity Ωm
S4	Mn	0.175	0.025	0.01	1.97×10^{11}
SU1A	U	0.175	0.025	0.0048	1.22×10^{10}
SU5A	U	0.175	0.025	0.0059	3.64×10^{9}
SU4A	U	0.175	0.025	0.0077	8.2×10^{8}
SU2A	U	0.175	0.025	0.011	2.26×10^{8}
SU3A	U	0.175	0.025	0.0145	1.02×10^{8}

Table 4

Resistivity Properties of Uranium-substituted compositions

4 Brief Description of Drawings

Figure 1 is a ternary phase diagram for PZ-PT-PMN showing compositions described by H. Ouchi, K. Nagano and S. Hayakāwa in the paper described (Ouchi 1995), and showing compositions described in other papers discussed above; and

Figure 2 is a ternary phase diagram for PZ-PT-PMN showing the regional specified in formula (4) above and the regions specified in formula (5) above.

【図１】

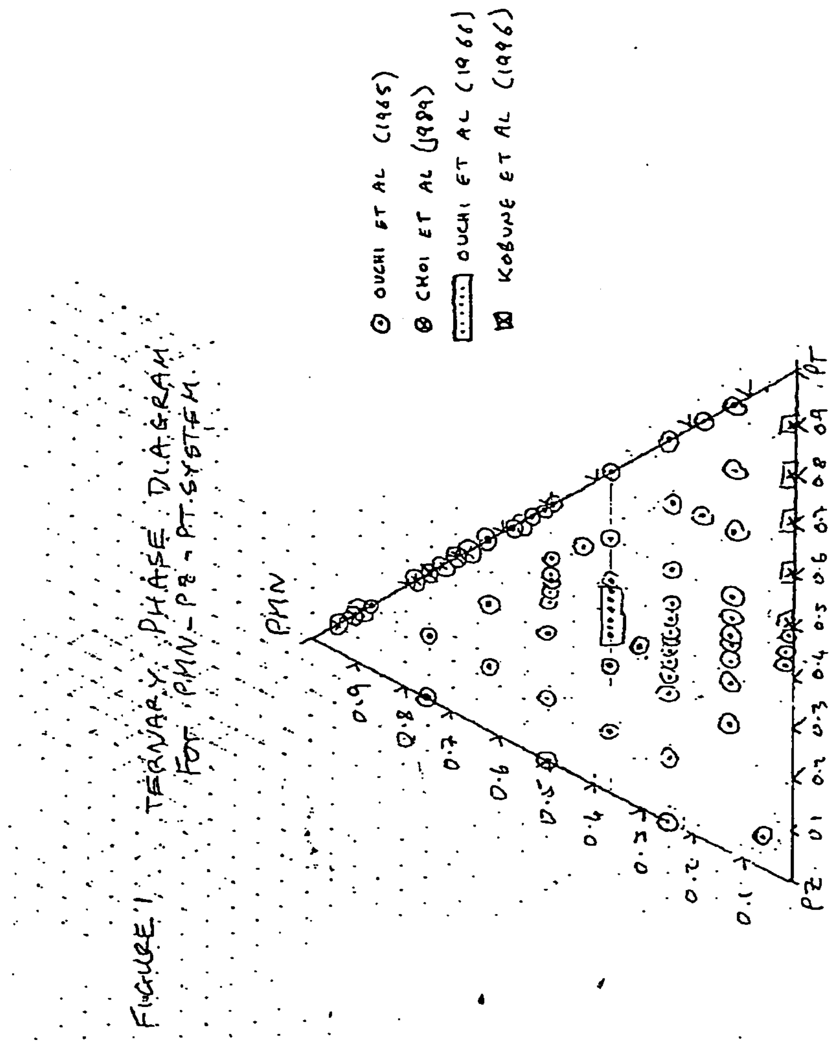
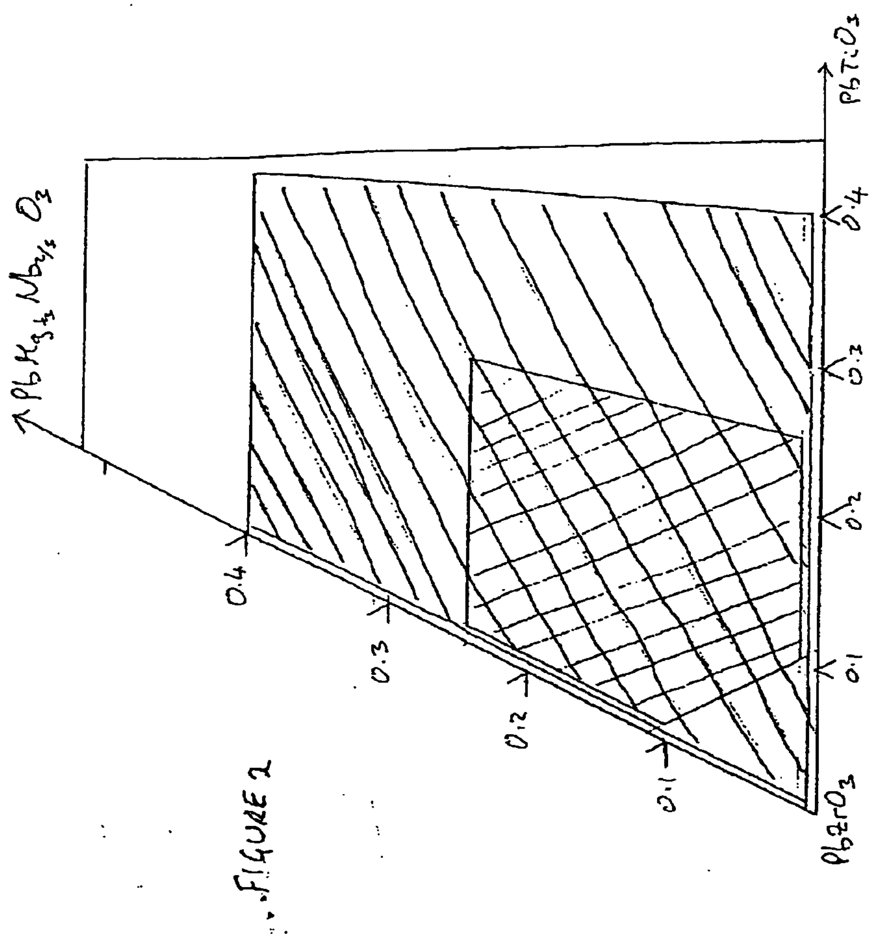


FIGURE 1 TERNARY PHASE DIAGRAM FOR PMN-PZ-PT SYSTEM
OUCHI ET AL (1965)
CHOI ET AL (1989)
OUCHI ET AL (1966)
KOBUNE ET AL (1996)
PMN
PT
PZ

【図２】



1 Abstract

A ferroelectric ceramic for use as a pyroelectric, said ceramic having the composition:

$Pb_{1+\delta}\{[(Mg_{1/3}Nb_{2/3})_y\ (Zr_{1-x}Ti_x)_{1-y}]_{1-z}A_z\}O_3$

where: $0.05 \geq \delta \geq 0$

$0.4 \geq x > 0$

$0.4 \geq y > 0$

$0.05 \geq z > 0$

and wherein A is a cationic multivalent octahedral site substituent.

The ferroelectric ceramic is useful as an active pyroelectric material in infrared detecting devices.

2 Representative Drawing

Fig. 2